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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: POLYMERIC FILMS WITH LOW WATER VAPOR TRANSMISSION RATES

$\text{CALC EX } \text{WVTR} = 314.45 - (650.45 \cdot \text{DENS}) + (336.5 \cdot \text{DENS}^2)$   
 $\text{CALC ZN } \text{WVTR} = 614.33 - (1285.16 \cdot \text{DENS}) + (672.44 \cdot \text{DENS}^2)$   
 $\square \text{ ACTUAL EX } \quad \triangle \text{ ACTUAL ZN}$

(57) Abstract

The disclosure concerns certain classes of non-polar hydrocarbon polymers, their production and use. The polymers of the invention are well suited for use in producing films having unique combinations of properties, especially low water vapor transmission rate.

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**TITLE: POLYMERIC FILMS WITH LOW WATER VAPOR  
TRANSMISSION RATES**

10 **FIELD OF THE INVENTION**

This invention relates generally to films. More specifically this invention is directed toward films having low vapor transmission rates, specifically a low water vapor transmission rate.

15 **BACKGROUND OF THE INVENTION**

Polymers exhibiting low permeability are generally referred to as barrier polymers. The major use of these barrier polymers is in the packaging industry, especially in packaging applications for foods and beverages. The driving force behind the increased market penetration by barrier plastics are that they are light weight, strong, easily disposed of by incineration, and of low costs.

20 The functional requirement of a package is to protect its contents from the environment over the normal shelf life of the product contained therein. The package may be a rigid container, a flexible container like a pouch or a non-barrier article with a barrier coating. In most food packaging applications protection from oxygen can be of great importance as can protection from the entry of moisture. 25 Moisture would cause dry soluble powders to cake or a loss of moisture may adversely affect the viscosity of water based liquids. Loss of moisture in food applications is especially important in keeping food fresh for an extended period of time.

30 In order to provide a useful packaging material the polymer must also have other attributes including: sufficient strength to form a durable package, with good impact and tear strength; resistance to puncture; good clarity when desirable; packaging processability; ability to withstand heat processing such as hot filling and pasteurization; anti-static properties; general chemical resistance including 35 resistance to environmental stress cracking, sealability and organoleptic properties.

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Thus, it is important that a good barrier polymer must have some of the more important of these properties such as tensile strength, toughness or impact resistance and optical properties as well as have low permeability.

The process of permeation through a polymeric barrier generally involves four steps: absorption of the permeating species into the polymer wall; solubility in the polymer matrix; diffusion through the wall along a concentration gradient; and desorption from the outer wall. There are certain molecular structures that lead to good barrier properties in polymers. A practical problem, however, is that the property might result in a good gas barrier but a poor water barrier or a good water barrier but poor strength and optical properties. For example, highly polar polymers, those having many hydroxyl groups for example, poly(vinyl alcohol) or cellophane are excellent gas barriers but are amongst the poorest water barriers. Conversely, very non-polar hydrocarbon polymers such as polyethylene have good water barrier properties but are poor gas barriers. For the purposes of this patent specification the barrier polymers of this invention are those non-polar hydrocarbon polymers.

Moisture transmission rates (MTR) or water vapor transmission rates (WVTR) depend generally on the crystallinity or density of the polymer. High density polyethylene (HDPE) usually has a density in the range of 0.945 g/cm<sup>3</sup> to 0.960 g/cm<sup>3</sup>. HDPE is generally linear without any side chain branching and is substantially crystalline. HDPE because of its highly crystalline structure has a low water transmission rate but poor optical, tear strength and seal strength properties. At the other end of the density or crystallinity spectrum are those polymers generally known as very low density polyethylene (VLDPE). VLDPE's generally have a density below to 0.915 g/cm<sup>3</sup>. VLDPE's at the low end of the spectrum are substantially amorphous and thus lack the desired stiffness property necessary for making films. However, VLDPE's have high water vapor transmission rates.

In the past, fillers or additives such as impact modifiers or plasticizers were used to lower vapor transmission rates. However, this resulted in added costs and affected other important properties necessary to the packaging industry. Therefore, a need exists for a barrier polymer from which a film having low transmission rates without the need for fillers or additives can be made such that the film also has a balance of desirable physical properties.

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### SUMMARY OF THE INVENTION

It has been discovered that metallocene catalyst systems can be used to produce polymers having not only excellent strength, sealing and optical properties but having superior water vapor transmission rates. These polymers or barrier polymers of the invention are particularly well suited for use in the packaging industry, specifically in those applications in which low water vapor transmission rates are desirable.

The invention is directed toward a polymer film comprising at least one resin layer. This layer has a density less than  $0.935 \text{ g/cm}^3$ , a  $M_w/M_n$  less than 3, a composition distribution breadth index greater than 80%; and said resin characterized in that at a density of  $0.90 \text{ g/cm}^3$  said film has a water vapor transmission rate less than  $2.25 \text{ g/mil/100 in}^2 \text{ day}$ . The film is either a single layer or multilayer film and can be coextruded, laminated or blended with other materials.

### BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing aspects, features and advantages of the invention will become clearer and more fully understood when the following detailed description is ready in conjunction with the accompanying drawings, in which

Figure 1 illustrates water vapor transmission rates as a function of density comparing films of this invention made with metallocene catalysts with those films made from resins produced by Ziegler-Natta catalysts.

Figure 2 is a DSC curve for the polymers of this invention and shows a single melting peak.

Figure 3 is a DSC curve for a prior art material showing multiple melting peaks.

### DETAILED DESCRIPTION OF THE INVENTION

#### Introduction

This invention concerns certain classes of non-polar hydrocarbon polymers specifically polyethylene resins, their production into film and applications in which films having a low water vapor transmission rates are desirable. These resins have unique properties particularly well suited for use in producing certain classes of polymeric films.

Principally, these resins are used primarily in packaging applications, specifically those applications requiring good water vapor transmission rates, for

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example, food and chemical packaging. The resulting films have combinations of properties rendering them superior to resins previously available. Some of these resins have been placed into commerce under the trade names EXACT 3001, 3025, 3024, 3026, 3027, 3028, 4011, 2009, 2010, 3006 and 3016 all available from Exxon Chemical Company, Houston, Texas.

Up until now it was not known or disclosed that these resins and others of this invention when converted into films would surprisingly and unexpectedly have low water vapor transmission rates. Following is a detailed description of certain preferred resins within the scope of this invention, preferred methods of producing these resins and preferred applications of these resins. Those skilled in the art will appreciate that numerous modifications to these preferred embodiments can be made without departing from the scope of the invention.

We have discovered that certain metallocene catalyst systems produce polymer resins that are highly desirable for use in certain film applications.

Generally, these resins have a very narrow molecular weight distribution and composition distribution than polymers produced from conventional Ziegler catalysts.

#### Production of the Resins

The polymer resins of this invention are produced using metallocene catalyst systems in a polymerization or copolymerization process in gas, slurry solution or high pressure phase.

The process for polymerizing or copolymerizing involves the polymerization of one more of the alpha-olefin monomers having from 2 to 20 carbon atoms, preferably 2-15 carbon atoms. The invention is particularly well suited to the copolymerization reactions involving the polymerization of one or more of the monomers, for example alpha-olefin monomers of ethylene, propylene, butene-1, pentene-1, 4-methylpentene-1, hexene-1, octene-1, decene-1 and cyclic olefins such as styrene. Other monomers can include polar vinyl, dienes, norbornene, acetylene and aldehyde monomers. Preferably a copolymer of ethylene is produced such that the amount of ethylene and comonomer is adjusted to produce a desired polymer product. Preferably the comonomer is an alpha-olefin having from 3 to 15 carbon atoms, preferably 4 to 12 carbon atoms and most preferably 4 to 10 carbon atoms. In another embodiment ethylene is polymerized with at least two comonomers to form a terpolymer and the like. If a comonomer is used then the monomer is generally polymerized in a proportion of 70.0-99.99, preferably 70-90 and more preferably 80-95 or 90-95 mole percent of monomer

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with 0.01-30, preferably 3-30 and most preferably 5-20, 5-10 mole percent comonomer.

For the purposes of this patent specification the term "metallocene" is defined to contain one or more cyclopentadienyl moiety in combination with a transition metal of the Periodic Table of Elements. The metallocene catalyst component is represented by the general formula  $(Cp)_mMR_nR'_p$  wherein  $Cp$  is a substituted or unsubstituted cyclopentadienyl ring;  $M$  is a Group IV, V or VI transition metal;  $R$  and  $R'$  are independently selected halogen, hydrocarbyl group, or hydrocarboxyl groups having 1-20 carbon atoms;  $m = 1-3$ ,  $n = 0-3$ ,  $p = 0-3$ , and the sum of  $m + n + p$  equals the oxidation state of  $M$ . Various forms of the catalyst system of the metallocene type may be used in the polymerization process of this invention. Exemplary of the development of these metallocene catalysts for the polymerization of ethylene is found in the disclosure of U.S. Patent No. 4,871,705 to Hoel, U.S. Patent No. 4,937,299 to Ewen, et al. and EP-A-0 129 368 published July 26, 1989, and U.S. Patent Nos. 5,324,800, 5,017,714, and 5,120,867 to Welborn, Jr. all of which are fully incorporated herein by reference. These publications teach the structure of the metallocene catalysts and includes alumoxane as the cocatalyst. There are a variety of methods for preparing alumoxane of which one described in U.S. Patent 4,665,208. Other cocatalysts may be used with metallocenes, such as trialkylaluminum compounds; or ionizing ionic activators or compounds such as, tri (n-butyl) ammonium tetra (pentafluorophenyl) boron, which ionize the neutral metallocene compound. Such ionizing compounds may contain an active proton, or some other cation associated with but not coordinated or only loosely coordinated to the remaining ion of the ionizing ionic compound. Such compounds are described in EP-A-0 277 003 and EP-A-0 277 004 both published August 3, 1988 and are both herein fully incorporated by reference. Further, the metallocene catalyst component can be a monocyclopentadienyl heteroatom containing compound. This heteroatom is activated by either an alumoxane or an ionic activator to form an active polymerization catalyst system to produce polymers useful in this present invention. These types of catalyst systems are described in, for example, PCT International Publications WO 92/00333 published January 9, 1992, U.S. Patent Nos. 5,096,867 and 5,055,438, EP-A-0 420 436 and WO 91/ 04257 all of which are fully incorporated herein by reference. In addition, the metallocene catalysts useful in this invention can include non-cyclopentadienyl catalyst components, or ancillary ligands such as boroles or carbolides in combination with a transition



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metal. Additionally it is not beyond the scope of this invention that the catalysts and catalyst systems may be those described in U.S. Patent No. 5,064,802 and PCT publications WO 93/08221 and WO 93/08199 published April 29, 1993 all of which are herein incorporated by reference. All the catalyst systems described  
5 above may be, optionally, prepolymerized or used in conjunction with an additive or scavenging component to enhance catalytic productivity.

The catalyst particles in a gas phase process may be supported on a suitable particulate material such as polymeric supports or inorganic oxide such as silica, alumina or both. Methods of supporting the catalyst of this invention are described  
10 in U.S. Patent Nos. 4,808,561, 4,897,455, 4,937,301, 4,937,217, 4,912,075, 5,008,228, 5,086,025 and 5,147,949 and U.S. Application Serial Nos. 898,255, filed June 15, 1992 and 885,170, filed May 18, 1992, all of which are herein incorporated by reference. The preferred support method in a gas phase process is generally disclosed in U.S. Patent No. 4,937,301 and related U.S. patents which  
15 are listed above.

The preferred catalyst, catalyst system and process is described in detail in U.S. Patent No. 5,084,534 herein fully incorporated by reference.

#### Characteristics of the Resins

A key characteristic of the resins of the present invention is their  
20 composition distribution. As is well known to those skilled in the art, the composition distribution of a copolymer relates to the uniformity of distribution of comonomer among the molecules of the copolymer. Metallocene catalysts are known to incorporate comonomer very evenly among the polymer molecules they produce. Thus, copolymers produced from a catalyst system having a single  
25 metallocene component have a very narrow composition distribution - most of the polymer molecules will have roughly the same comonomer content, and within each molecule the comonomer will be randomly distributed. Ziegler-Natta catalysts, on the other hand generally yield copolymers having a considerably broader composition distribution. Comonomer inclusion will vary widely among  
30 the polymer molecules.

A measure of composition distribution is the "Composition Distribution Breadth Index" ("CDBI"). CDBI is defined as the weight percent of the  
35 copolymer molecules having a comonomer content within 50% (that is, 25% on each side) of the median total molar comonomer content. The CDBI of a copolymer is readily determined utilizing well known techniques for isolating individual fractions of a sample of the copolymer. One such technique is

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Temperature Rising Elution Fraction (TREF), as described in Wild, et al., J. Poly. Sci., Poly. Phys. Ed., vol. 20, p. 441 (1982) and U.S. Patent No. 5,008,204, which are incorporated herein by reference.

5 To determine CDBI, a solubility distribution curve is first generated for the copolymer. This may be accomplished using data acquired from the TREF technique described above. This solubility distribution curve is a plot of the weight fraction of the copolymer that is solubilized as a function of temperature. This is converted to a weight fraction versus composition distribution curve. For the purpose of simplifying the correlation of composition with elution temperature the weight fractions less than 15,000 are ignored. These low weight fractions  
10 generally represent a trivial portion of the resin of the present invention. The remainder of this description and the appended claims maintain this convention of ignoring weight fractions below 15,000 in the CDBI measurement.

15 From the weight fraction versus composition distribution curve the CDBI is determined by establishing what weight percent of the sample has a comonomer content within 25% each side of the median comonomer content. Further details of determining the CDBI of a copolymer are known to those skilled in the art. See, for example, PCT Patent Application WO 93/03093, published February 18, 1993.

20 The resins of the present invention have CDBI's generally in the range of 80-98%, usually in the range of 85-98% and most typically in the range of 90-95%. Obviously, higher or lower CDBI's may be obtained using other catalyst systems with changes in the operating conditions of the process employed.

25 The films of this invention are also distinguishable from known films made from Ziegler-Natta based resins on the basis of their molecular weight distribution (MWD). The MWD of the present resins is materially narrower than that of resins produced using traditional Ziegler-Natta catalysts. The polydispersity index ( $M_w/M_n$ ) of our resins is typically in the range of 1.5-3, compared to a range of 3 and above for most known Ziegler catalyzed resins. In this regard the present  
30 resins are very different from many commercially available resins produced using Ziegler-Natta catalysts. In addition, the tails of the molecular weight distribution curve for the present resin are considerably smaller than those of known Ziegler-Natta LLDPEs. This distinction is readily apparent by comparing the ratio of  $M_z/M_w$  (the ratio of the third moment to the second moment) and  $M_{z+1}/M_w$   
35 (ratio of the fourth moment to the second moment). Utilizing the present invention, resins can be produced with an  $M_z/M_w$  less than 2.5, usually less than

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2.0 and most typically in the range of 1.4 - 1.9. In contrast, the ratio of  $M_z/M_w$  for Ziegler-Natta resins is typically above 2.5. Similarly, the value of  $M_{z+1}/M_w$  for the present resins is less than 4.0, usually less than 3.0 and most typically in the range of 2.0-3.0. For Ziegler-Natta resins  $M_{z+1}/M_w$  is generally much higher - typically above 4.0. Table I provides further data regarding  $M_z$ ,  $M_w$ ,  $M_{z+1}$  for the resins of this invention and also for some commercially available resins.

Those skilled in the art will appreciate that there are several methods available for determining the molecular weight distribution of a polyethylene sample. For the purpose of Table I and other reference to  $M_w$ ,  $M_z$  and  $M_{z+1}$  given in this application and the appended claims, molecular weight distribution is determined with a Waters Gel Permeation Chromatograph equipped with ultrastyro gel columns operated at 145°C. Trichlorobenzene is used as the eluting solvent. The calibration standards are sixteen polystyrenes of precisely known molecular weight, ranging from a molecular weight of 500 to a molecular weight of 5.2 million. NBS 1475 polystyrene was also used as a calibration standard.

The melt index of the resins of the invention are generally in the range of 0.1 to 1000 dg/min, preferably 0.1 to 100 dg/min, more preferably 0.1 to 20 dg/min and even more preferably 0.1 to 10 dg/min and most preferably 0.1 to 5 dg/min.

#### Properties of films produced from the resins

The resins produced using the metallocene catalyst described above are in many applications markedly superior to commercially available products. These resins are particularly useful in film applications. Tables I and II set forth the properties of films of this invention (resin A-J) of the present invention and compares these properties to the corresponding properties of films produced several commercially available resins derived from conventional Ziegler-Natta catalysts.

For the purposes of this patent specification all tests were run on a 2 1/2" blown film line. The extruder was a 24/1 L/D and was powered by a 40 hp DC motor, the overall reduction ratio was 15.22:1 giving a maximum screw speed of 115 rpm. The cylinder and screw showed virtually no wear. The screw was a dual channel barrier mixing screw with Maddock mixer at the tip designed for LLDPE extrusion. (Feed section -- 4 1/2 diameters long with 0.50" depth channels, Barrier section -- 13 diameters long with 0.165" wide flights and 0.050" clearance; Metering section -- 4 diameters long with 0.210" deep channels; Mixer -- 2 1/2

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diameters long with 3 channels, 0.050" clearance and 0.375" wide barriers.) A 20/80/100/20 mesh screen pack was used for all test runs.

A state-of-the-art die system was used, including a 6" multi-ported low pressure spiral mandrel die with a 1/2" die land. Mandrel extensions for 60 mil die gaps were used, all with parallel die lands. The air ring was a duel orifice air ring employing a forming cone of 6" height and 11" top diameter.

Temperature Profile	Max Set	Min Set
Barrel Zone #1, °F	300	300
Barrel Zone #2, °F	400	390
Barrel Zone #3, °F	380	355
Adapt. Conn. Pipe, °F	390	355
Die Adapter, °F	390	365
Die Zone #1, °F	390	365
Die Zone #2, °F	390	365
Die Zone #3, °F	390	365
Pressure Profile		
Extruder Head Pressure, psi	358	2770
Extruder Speed, rpm	57	48
Air Ring Pressure in H <sub>2</sub> O	4.4	2.7
Air Ring Temp, °F	50	48
Line Speed, fpm	121	101
Lay Flat Width, in	19	19
Gauge, mils	1.250	1.250

Further details of the process above is found in the paper, Kurzbuch, "LLDPE Blown Film Productivity: Effects of Processing Temperatures and Die Gap on Attainable Production Rates", Journal of Plastic Film & Sheeting, Vol. 3, April, 1987, which is herein incorporated by reference.

Blown films tend toward a lower water vapor transmission rate as compared with cast films at the same density. All the tests herein were conducted on blown films.

The resins of this invention have lower WVTR than traditional Ziegler-Natta produced materials at the same or similar density. This can best be seen in

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Figure 1 which plots WVTR as a function of density. For the purposes of this patent specification WVTR tests were performed on a MOCON permatron developed by Modern Controls, Inc. using ASTM F 372-73 at 100°F (378°C) and 100% relative humidity.

5 The WVTR's of the films of the invention are generally in the range of 0.5 g mil/100 in<sup>2</sup>/day to 3.0 g mil/100 in<sup>2</sup>/day. Preferably are film having a WVTR in the range of 0.5 g mil/100 in<sup>2</sup>/day to 2.5 g mil/100 in<sup>2</sup>/day and more preferably in the range of 0.55 g mil/100 in<sup>2</sup>/day to 2.0 g mil/100 in<sup>2</sup>/day. This particular attribute is most pronounced in films having a density less than 0.940 g/cm<sup>3</sup>,  
 10 preferably less than or equal to 0.935 g/cm<sup>3</sup> and a density greater than 0.860 g/cm<sup>3</sup>, preferably greater than 0.88 g/cm<sup>3</sup>. Most preferred are films having densities in the range of 0.865 g/cm<sup>3</sup> to 0.940 g/cm<sup>3</sup>, preferably 0.87 g/cm<sup>3</sup> to 0.935 g/cm<sup>3</sup>, most preferably 0.88 g/cm<sup>3</sup> to less than 0.935 g/cm<sup>3</sup>, most preferably 0.900 g/cm<sup>3</sup> to 0.930 g/cm<sup>3</sup> and even most preferably .900 g/cm<sup>3</sup> to  
 15 0.915 g/cm<sup>3</sup>.

In one embodiment where the resin of the invention is characterized in that at a density of 0.90 g/cm<sup>3</sup> said film has a WVTR less than 2.25 g mil 100 in<sup>2</sup>/day, preferably the WVTR is less than 2.0 g mil/100 in<sup>2</sup>/day, more preferably less than 1.75 g mil/100 in<sup>2</sup>/day and most preferably less than 1.5 g mil/100 in<sup>2</sup>/day.

20 In yet another embodiment the resin is characterized in that at a density of 0.91 g/cm<sup>3</sup> said film has a WVTR less than 1.5 g mil/100 in<sup>2</sup>/day, most preferably less than 1.4 g mil/100 in<sup>2</sup>/day.

In still another embodiment the resin is characterized in that at a density of 0.912 g/cm<sup>3</sup> said film has a WVTR is less than 1.55 g mil/100 in<sup>2</sup>/day preferably  
 25 less than 1.5 g mil/100 in<sup>2</sup>/day.

In one embodiment the WVTR for the films of this invention are represented by the following general empirical formula derived from Figure 1:

$$\text{WVTR} = 314.43 - (650.45 \times D) + (336.5 \times D^2)$$

where D is the density. Films made from resins of traditional Ziegler-Natta materials generally follow the following empirical formula:

30 
$$\text{WVTR}^1 = 614.33 - (1285.16 \times D) + (672.44 \times D^2)$$

where D is the density. Thus, at a given density less than about 0.935 g/cm<sup>3</sup> WVTR will be less than WVTR<sup>1</sup>.

A particular attribute of the present resins is their very low level of  
 35 extractable components. The extractables level for most grades of resins are in the range of between 5.5% to below 0.1%, preferably below 2.6%, more preferably

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below 1.0%, even more preferably below 0.8% and most preferably below 0.5%. The extractables level of our resins generally increases with decreasing molecular weight and decreasing density. At any given molecular weight and density (or side chain branching) our resins have an extractables level significantly below that of the counterpart Ziegler-Natta grade. For the purposes of this specification and the appended claims, the extractables level is measured by exposing film produced from the resin to n-hexane at 50°C for 2 hours. This process is further detailed in 21 CFR 177.1520 (d)(3)(ii) an FDA requirement. It will be appreciated by those skilled in the art, that the extractables test is subject to substantial variation. The variations may be due to film thickness (4 mils maximum) or any other variable that changes the surface to volume ratio. Film fabrication type (e.g. blown, cast) and processing conditions may also change the extractable amount. The low extractables of films produced from these resins makes them well suited for food applications.

Films produced from the present resins also have excellent optical properties. The excellent optics can be seen from Table II.

The excellent tensile strength, impact strength and puncture properties of the present resins permit resin density to be raised as required to achieve the desired film stiffness and/or yield strength without reducing toughness below acceptable levels for most applications. This superior toughness/stiffness balance has significant benefit by permitting simplified film formulations for applications requiring yield strength as well as excellent water vapor transmission rates.

Another important property of the films produced in accordance with this invention is their very high impact strength. Dart impact strengths above 1000 g/mil may be easily obtained. Indeed, many grades have dart impact strengths above 1500 g/mil. Dart impact strengths for the films of this invention are in the range of about 100 g/mil to greater than 1500 g/mil, preferably greater than 400 g/mil to more preferably greater than 900 g/mil and most preferably greater than 1000 g/mil.

It is not beyond the scope of the invention to blend the resins of the films of the invention with other materials such as LLDPE, LDPE, HDPE, PP, PB, EVA, SBS and the like. The films of the invention include blown or cast films in mono-layer or multilayer construction formed by coextrusion or lamination.

The resin and product properties recited in this specification were determined in accordance with the following test procedures. Where any of these

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properties is referenced in the appended claims, it is to be measured in accordance with the specified test procedure.

Property	Units	Procedure
Melt Index	dg/min	ASTM D-1238(E)
Density	g/cc	ASTM D-1505
Haze	%	ASTM D-1003
Gloss @ 45°	%	ASTM D-2457
Tensile @ Yield	psi	ASTM D-882
Elongation @ Yield	%	ASTM D-882
Tensile @ Break	psi	ASTM D-882
Elongation @ Break	%	ASTM D-882
1% Secant Modulus	kpsi	ASTM D-882
Dart Impact Strength	g/mil	ASTM D-1709
Elmendorf Tear Resistance	g/mil	ASTM D-1922
Puncture Force	lb/mil	ASTM D-3763
Puncture Energy	in-lb/mil	ASTM D-3763
Puncture Propagation Tear Resistance (PPT)	kgf	ASTM D-2582
Total Energy Impact	ft-lb	ASTM D-4272
Reblock	g	ASTM D-3354
Water Vapor Transmission Rate	g mil/100 in <sup>2</sup> /day	ASTM F 372-73

- 5 While the present invention has been described and illustrated by reference to particular embodiments thereof, it will be appreciated by those of ordinary skill in the art that the invention lends itself to variations not necessarily illustrated herein. For example, it is not beyond the scope of this invention to include additives with the claimed films or to blend or coextrude the claimed films with
- 10 other polymers or even laminate the claimed films to other materials such as metal foils, paper, other polymer films and the like. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

TABLE I  
COMPARISON OF  $M_w$  AND  $M_{z+1}$  AND CDBI

Product	MI	Density (g/cc)	Comonomer	Extract	$M_w$ ( $\times 10^{-3}$ )	$M_z$ ( $\times 10^{-3}$ )	$M_{z+1}$ ( $\times 10^{-3}$ )	$M_w/M_z$	$M_{z+1}/M_w$	CDBI	WVTR
Resin A	1.2	0.900	C4	1.1	98.9	149.5	202.7	1.51	2.05	94	1.73
Resin B	1.2	0.900	C6	—	107.0	160.8	222.2	1.50	2.08	—	1.86
Resin C	2.2	0.905	C4	0.6	84.5	131.8	181.8	1.56	2.15	95	1.48
Resin D	2.2	0.905	C6	—	77.6	120.1	163.6	1.55	2.11	93	1.25
Resin E	1.2	0.910	C4	—	100.4	155.9	215.2	1.55	2.14	94	1.24
Resin F	1.2	0.910	C4/C6	—	95.6	156.5	235.1	1.64	2.46	—	1.39
Resin G	1.05	0.911	C6	—	103.4	168.0	248.3	1.62	2.40	—	—
Resin H	2.4	0.920	C6	0.5	81.0	133.1	188.6	1.64	2.33	94	—
Resin I	1.4	0.920	C6	0.3	93.3	150.8	213.8	1.62	2.29	95	—
Resin J	1.5	0.924	C6	0.2	93.2	149.5	214.2	1.61	2.30	—	0.87
Dowlex 2045	1.0	0.92	C8	0.8	119.7	378.4	800.5	3.16	6.69	56	1.11
Dowlex 2045.02	1.0	0.92	C8	—	101.2	313.8	696.0	3.10	6.88	—	—
Dowlex 2045A	1.0	0.92	C8	—	112.3	351.3	694.7	3.13	6.19	—	—
Dowlex NG	1.0	0.92	C8	—	114.6	360.9	717.8	3.15	6.26	52	—
Mobil NTX-101	0.9	0.919	C6	—	118.2	312.9	583.4	2.65	4.94	23	—
Attane 4201	1.0	0.912	C8	1.9	120.3	385.3	710.0	3.20	5.90	46	1.58
Escorene LL-1001	1.0	0.918	C4	2.6	102.2	270.8	529.7	2.65	5.18	—	1.19
Escorene LL-3001	0.9	0.919	C6	3.7	116.4	342.7	655.5	2.94	5.63	20	1.26
Escorene LL-3003	3.2	0.919	C6	—	80.7	242.3	518.6	3.00	6.42	34	—
Escorene LL-3003	4.3	0.920	C6	—	74.6	232.0	505.1	3.11	6.77	45	—
Escorene LL-3003	3.9	0.919	C6	—	76.7	227.4	473.4	2.96	6.17	56	—
Escorene LL-3003	3.6	0.920	C6	—	78.5	232.8	506.0	2.96	6.44	34	—



TABLE II  
TYPICAL BLOWN FILM PROPERTIES (2.5" EGAN/60 MIL DIE GAP)

Grade	Units	D	Attane 4201 VLDPE	LL-1001 LLDPE	LL-3001 LLDPE	Resin E Butene	Resin A Butene	Resin B Hexene
Comonomer	—							
Density	G/CC		912	0.918	0.918	0.9102	0.9012	0.9001
Melt Index	G/10°		1	1	1	1.16	1.17	0.93
Gauge Average	MIL		1.21	1.42	1.24	1.35	1.34	1.36
1% Secant Modulus	PSI	MD	23150	30140	33370	16940	10630	11930
Tensile @ Yield	PSI	TD	27320	35550	40650	18050	10800	12900
Elongation @ Yield	PSI	MD	1134.2	1305.5	1381.3	984.8	663.3	707
Elongation @ Break	PSI	TD	1112.4	1407.4	1571.2	929.2	613.8	654
Ultimate Tensile	PSI	MD	6.07	6.06	5.91	6.91	8.37	7.6
	%	TD	5.46	5.81	5.74	6.85	7.69	7.35
	%	MD	488.3	598.3	565.3	645	593	442
	%	TD	687.8	769	721.8	665.3	679.2	542
	%	MD	8514	6831	8228.3	8140.8	8669.3	10748
	PSI	TD	7107.8	4816	6253.3	5675.5	7245	9606
Shrink	%	MD	57	49	36	57	33	40
Elmendorf Tear	%	TD	-6	-15	-6	-12	4	-1
Dart Impact	g/mil	MD	379	118.5	244.2	111.4	122.7	152
Puncture Force	g/mil	TD	659.4	412.3	641.1	236.7	176.9	250
Puncture Energy	lbs/mil		803.8	92.9	114.5	>1050	>1057.5	>1042
Haze	in"lbs/mil		7.44	5.7	5.75	5.94	7	8.52
Gloss	%		22.57	10.97	13.83	14.33	21.1	27.26
Total Energy Impact	%		8.4	13.6	15.5	3.7	3.1	0.6
	%		59.1	45.8	38.4	78.9	82.6	94.6
	R/lbs	23C	4.2	1.085	1.784	2.137	>6.16	>6.16
	R/lbs	-34C	---	0.685	0.734	1.736	2.16	3.49
WVTR	g mil/100 in <sup>2</sup> /day		1.58	1.19	1.26	1.24	1.73	1.86

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CLAIMS

I Claim:

1. A polymeric film having improved water vapor transmission rate comprising at least one resin layer, said layer having a density in the range of 0.860 g/cm<sup>3</sup> to 0.935 g/cm<sup>3</sup>, a Mw/Mn less than 3, a Mz/Mw less than 2.0, a CDBI greater than 80% and said resin layer is characterized in that at a density of about 0.90 g/cm<sup>3</sup> said film has a WVTR less than 2.25 g mil/100 in<sup>2</sup>/day.
2. A polymeric film comprising at least one layer, said layer having a density less than 0.935 g/cm<sup>3</sup> and said film having a WVTR such that the following formula is generally satisfied:  
$$\text{WVTR} = 314.54 - (650.45 \times D) + (336.5 \times D^2)$$
where D represents density of said layer.
3. A polymeric film comprising at least one layer comprising a density less than 0.935 g/cm<sup>3</sup> and said film having a WVTR less than the WVTR<sup>1</sup> using the following formula:  
$$\text{WVTR}^1 = 614.33 - (1285.16 \times D) + (672.44 \times D^2)$$
where D represents density of said layer.
4. The polymeric film of any preceding claim wherein said layer has a CDBI greater than about 90%.
5. The polymeric film of any preceding claim wherein said layer has a density in the range of less than about 0.88 g/cm<sup>3</sup> to about 0.92 g/cm<sup>3</sup>.
6. The polymeric film of any preceding claim wherein said layer has a single melting peak.
7. The polymeric film of any preceding claim wherein said film has a WVTR less than about 2.0 g mil/100in<sup>2</sup>/day, preferably less than 1.75 g mil/100 in<sup>2</sup>/day.
8. The polymeric film of any preceding claim wherein said film has a dart impact strength greater than 900 g/mil, preferably greater than 1000 g/mil.

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9. The polymeric film of any preceding claim wherein said film is blended with laminated to or coextruded with at least one other polymer.

5 10. The film of any preceding claim wherein said layer has a  $M_z/M_w$  less than 1.9.

11. The film of claim 3 wherein said WVTR is 80% of WVTR<sup>1</sup>.

10 12. An article of manufacture comprising the polymeric film of any preceding claim.

13. The article of claim 12 wherein said article is selected from one of the group consisting of bags, pouches, packages and containers.

15

FIG. 1

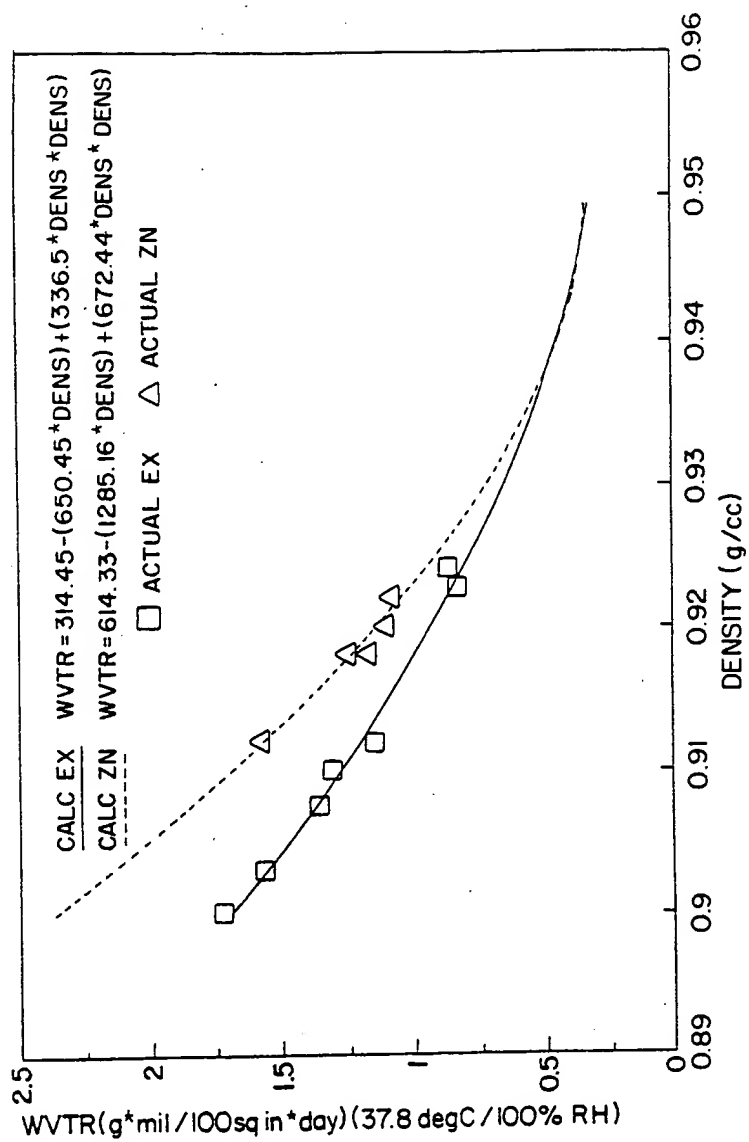


FIG. 2

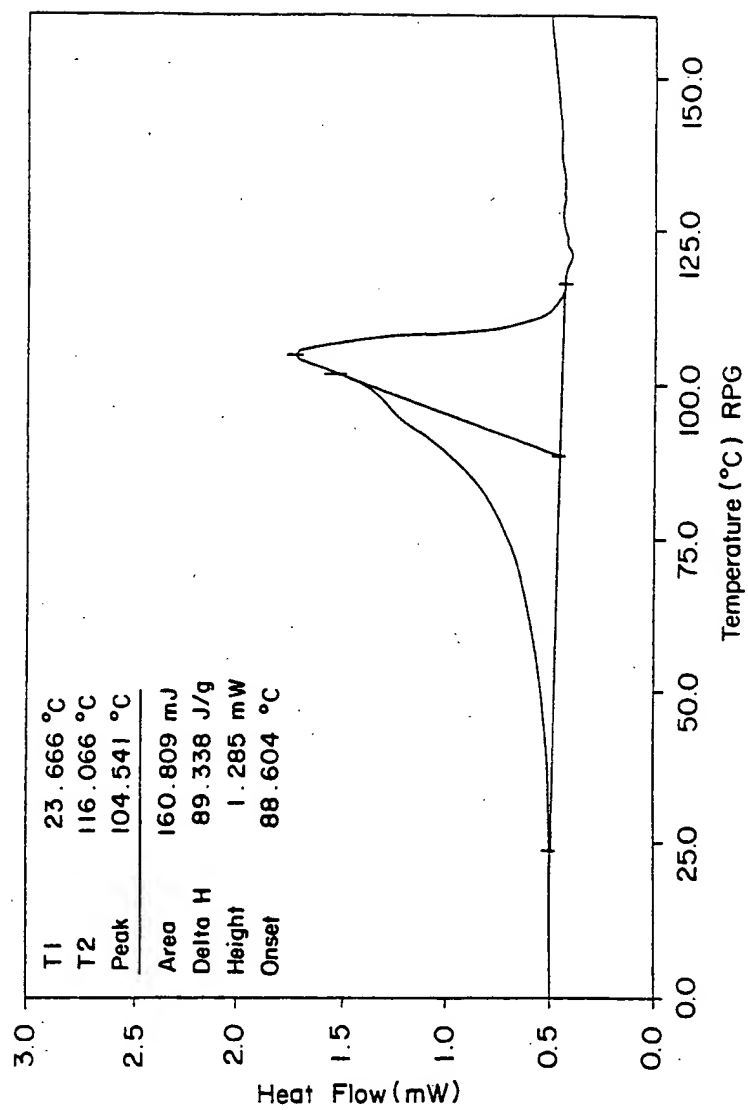
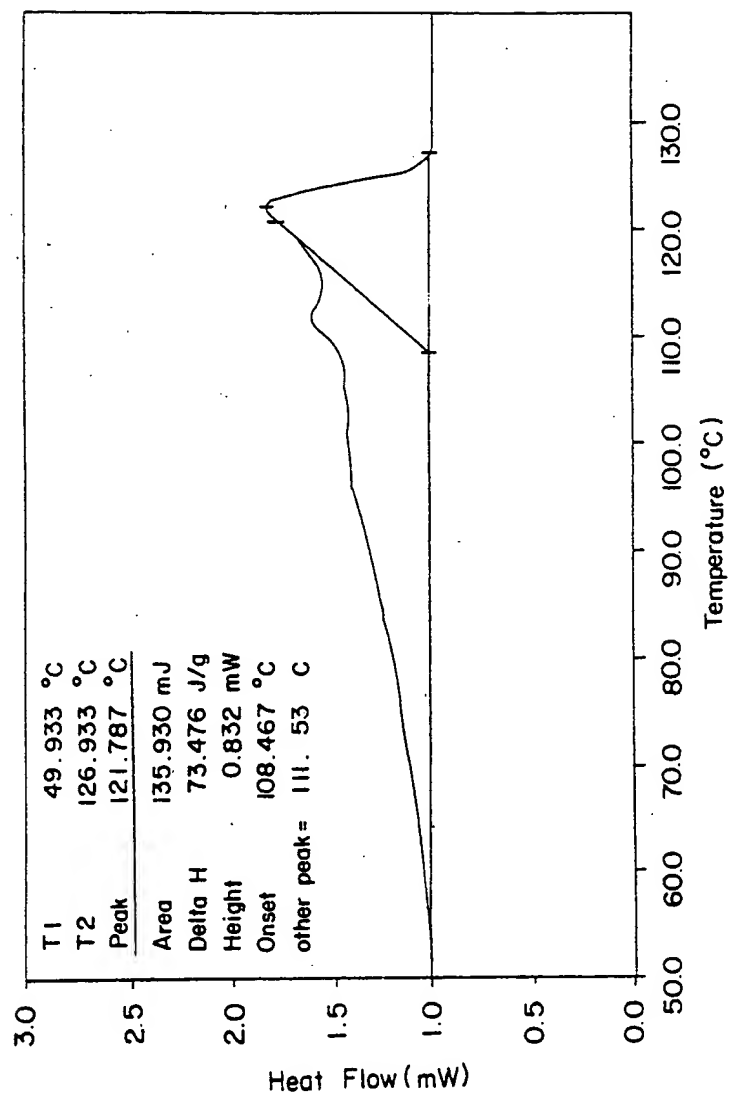


FIG. 3



# 1. INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 94/07553

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 6 C08J5/18 B29D7/01 //B29K23:00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 6 C08J B29D C08L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO, A, 92 14784 (EXXON CHEMICAL PATENTS) 3 September 1992 see table II ---	1-13
A	MODERN PLASTICS INTERNATIONAL, vol. 22, no. 11, November 1992, LAUSANNE pages 16 - 18 MARTINO R. 'New polyolefin resin emerge: "Branched linear" copolymers' ---	1-13
P, A	MODERN PLASTICS INTERNATIONAL, vol. 23, no. 10, October 1993, LAUSANNE page 99 'Packaging resins based on new "single site" catalysis' --- -/-	1-13
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "A" document member of the same patent family		
Date of the actual completion of the international search  12 October 1994		Date of mailing of the international search report  28. 10. 94
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2220 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016		Authorized officer  Attalla, G

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 94/07553

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	<p>MODERN PLASTICS INTERNATIONAL, vol. 23, no. 12, December 1993, LAUSANNE pages 16 - 17 MAPLESTON P. 'New versions of LLDPE may take share of LDPE market' -----</p>	1-13



Information on parent family members

PCT/US 94/07553

Form PCT/ISA/210 (patent family annex) (July 1992)